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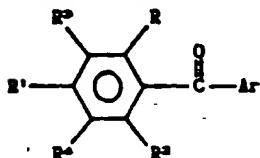
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(61) Substituted benzophenones and their liquid mixtures suitable for use as photopolymerisation initiators.

(67) As initiators for the photopolymerisation of ethylenically unsaturated compounds, the use of systems consisting of compounds of benzophenone type of formula I



I

In which R, R¹ and R² are preferably alkyls of 1-4 carbon atoms, R³ and R⁴ are preferably hydrogen and Ar is preferably phenyl, in combination with donors of hydrogen or substances which determine the formation of labile photochemical complexes, such as alcohols, ethers and tertiary amines with hydrogens in the alpha position, and the use for the same purpose of mixtures of 2,4,6-triethylbenzophenones and benzophenone and particularly of a mixture of 2,4,6-trimethylbenzophenone and benzophenone in a molar ratio of 1.155, which has the advantage of being liquid at temperatures exceeding 10°C and of possessing photochemical activity superior to that of benzophenone.

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SUBSTITUTED BENZOPHENONES AND THEIR LIQUID MIXTURES SUITABLE FOR
USE AS PHOTOPOLYMERISATION INITIATORS

This invention relates to the use of systems comprising
5 substituted benzophenones and their liquid mixtures as photopolymerisation initiators for ethylenically unsaturated compounds.

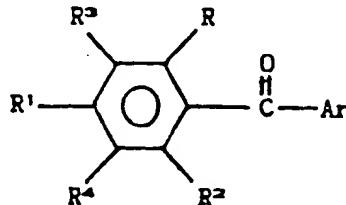
Ethylenically unsaturated compounds and in particular acrylic and
methacrylic acid derivatives can be polymerised by irradiation
10 with ultraviolet light of wavelength between 200 and 450 nm in
the presence of photoinitiator systems formed from:
A) benzophenone or its derivatives
B) a donor of hydrogen or substances which determine the
formation of a labile photochemical complex with the carbonyl
15 compound (A), such as alcohols, tertiary amines or ethers having
available hydrogens on the carbon adjacent to the heteroatom.

Examples of benzophenones which form these photoinitiator systems
are benzophenone itself which is the most widely used, 4,4'-bis
20 dimethyl(or diethyl) aminobenzophenone (Michler ketone), which is
very efficient in pigmented systems, 4-hydroxybenzophenone
condensed with ethylene oxide and esterified with acrylic acid,
which has the advantage of being liquid and copolymerisable, 2-
carbomethoxybenzophenone, 3,3',4,4'-benzophenonetetracarboxylic
25 acid esters etc. As many of these products are solid, they are
difficult to incorporate into the photopolymerisable systems, or
have a photochemical efficiency which is less than benzophenone
itself.

In accordance with the present invention, we have now surprisingly discovered that systems consisting of:

A) compounds of formula I

5



I

in which

10 R signifies linear or branched C_1-C_{12} alkyl possibly substituted with one or more phenyl, chlorine, bromine, C_1-C_{12} alkoxy, ArO^- , $ArSO^-$, $ArSO_2^-$, C_1-C_{12} alkylsulphinyl or C_1-C_{12} alkylsulphonyl groups; or $-SO_3H$ or C_1-C_{12} dialkylamino, respectively as free acids or bases or 15 salfied with organic or inorganic bases; C_1-C_{12} alkoxy; or ArO^-

15 R', R² which can be equal or different, each independently have the same meaning as R or represent hydrogen or a bridge of carbon atoms with Ar or R³ or R⁴ possibly comprising 20 heteroatoms

20 R³, R⁴ which can be equal or different, each independently represent hydrogen, linear or branched C_1-C_{12} alkyl, phenyl, chlorine, bromine, $-SO_3H$ possibly salfied with organic or inorganic bases, or $ArCO^-$

25 Ar represents a C_6-C_{10} aryl either non-substituted or carrying one or more substituents of the halogen, C_1-C_{12} alkyl, phenyl, C_1-C_4 alkoxy, C_3-C_6 cycloalkoxy, phenoxy, $-COOH$, C_1-C_6 alkoxycarbonyl, benzoyl, C_1-C_6 dialkylamino, C_1-C_6 alkylthio, alkylsulphinyl, alkylsulphonyl, 30 arylthio, arylsulphinyl and arylsulphonyl group; or 2,3 or 4-pyridyl; or a furan or thiophene residue

B) an organic tertiary amine of aliphatic type, or an ester of p-dimethylaminobenzoic acid or 4,4'-bis-(C_1-C_6 dialkylamino) benzophenone, or single or polymeric ethers of primary or 35 secondary alcohols or glycols or primary or secondary aliphatic alcohols or in any event donors of hydrogen or substances which determine the formation of labile chemical complexes,

can be used in the photoinitiated polymerisation of ethylenically unsaturated compounds, and in particular of acrylic and methacrylic acid derivatives, with a photochemical efficiency considerably greater than that of analogous systems containing 5 the currently used benzophenones indicated heretofore.

Further according to the invention, we have also surprisingly found that particular mixtures of benzophenone and compounds of formula I, by virtue of having melting points considerably lower 10 than those of the individual compounds, can be used in the liquid state with considerable practical advantages with regard to their incorporation into the photopolymerisable mixtures, in combination with the compounds of type B indicated heretofore.

15 Preferred systems for use according to the present invention are those consisting of:

A) one or more benzophenones of formula I in which R, R¹, R² which can be equal or different, each independently signify C₁-C₄ alkyl,

20 R³, R⁴ which can be equal or different, each independently signify hydrogen, C₁-C₄ alkyl, or -SO₃H possibly sulfided with organic or inorganic bases,

Ar signifies phenyl, possibly substituted with one or more C₁-C₄ alkyl, Cl, Br or C₁-C₄ alkylthio groups

25 B) an organic tertiary amine of aliphatic type, or an ester of p-dimethylaminobenzoic acid or 4,4'-bis-(C₁-C₄ dialkylamino) benzophenone, or molecules containing single or polymeric derivatives of glycols.

30 Examples of compounds of formula I are:

2,4,6-trimethylbenzophenone

2,4,6-triethylbenzophenone

2,4,6-triisopropylbenzophenone

2,4,6-tritert. butylbenzophenone

35 2,4,6-trimethoxybenzophenone

2,3,4,5,6-pentamethylbenzophenone

sodium 2,4,6-trimethylbenzophenone-3-sulphonate

4-(2,4,6-trimethylbenzoyl)pyridine

2-(2,4,6-trimethylbenzoyl)pyridine.

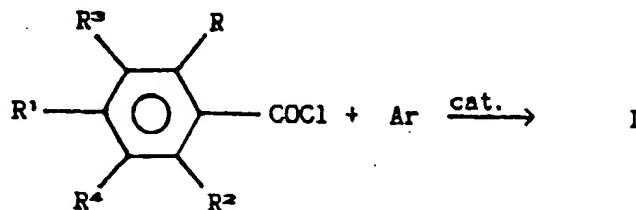
Preferred as liquid mixtures of compounds of formula I and
5 benzophenone are those with molar ratios of between 0.1 and 10.

Particularly preferred as liquid mixtures of compounds of formula
I and benzophenone are those of 2,4,6-trimethylbenzophenone and
benzophenone in molar ratios of between 1 and 1.3 having a pour
10 point less than 0°C.

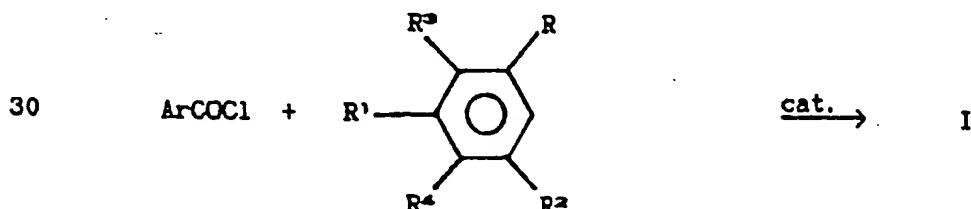
Particularly preferred compounds of type B are single polymeric
derivatives of aliphatic alkanolamines, esters of p-dialkyl-
aminobenzoic acid, and aliphatic alcohols and glycols possibly
15 carrying acrylic saturations or included in macromolecular
structures.

Compounds of formula I are known from the scientific literature
and are normally obtained by Friedel-Crafts acylation (Houben
20 Weyl, Methoden der Organischen Chemie, Band VII/2a, Teil 1, pag.
164-233) in accordance with the two following alternatives:

25



30



where cat. signifies a Friedel-Crafts catalyst. For example
2,4,6-trimethylbenzophenone has been obtained by acylation of
35 mesitylene with benzoyl chloride in the presence of anhydrous
aluminium chloride [Louise, Annales del Chemie, 6 (6) 202; H.O.
House et al., J. Org. Chem., 41, 3083 (1976)].

Although there are numerous publications in the literature on the photochemistry and photophysics of the compounds of formula I, and in particular of 2,4,6-trialkylbenzophenones (Y. Kitaura et al., Tetrahedron, 27 1597 (1971) - Y. Ito et al., J. Am. Chem.

5 Soc. 102, 5917 (1980), ibid. 105, 1590 (1983), J. Org. Chem., 46, 4359 (1981) - G. Porter et al., J. Chem. Soc. (A) 3772 (1971), Chem. Comm., 1372 (1970)] there is no reference to their use as polymerisation photoinitiators.

10 The photopolymerisable compounds with which the photoinitiator systems according to the present invention can be advantageously used are di, tri, tetra or polyfunctional monomers and oligomers of acrylic or methacrylic type, such as esters or amides.

15 Photopolymerisable oligomers and prepolymers are represented most commonly by polyester, polyether, polyurethane, acrylic, epoxy and silicone resins containing acrylic or methacrylic functionalities. Those mixtures useful in the art are those formed from the aforesaid monomers and oligomers in possible

20 combination with pigments, fillers, thermal stabilisers, light stabilisers, antioxidants, paraffins etc., various auxiliaries such as anti-foaming agents, dispersants etc. The co-use of other photoinitiators such as benzyl ketals, benzoin ethers, thioxanthones etc. is also possible.

25

Photopolymerisable mixtures containing the photoinitiator systems according to the present invention can be used as coatings for wood, metal, paper, fabrics, plastics materials, fibreglass, rubber; printing inks, adhesives and sealants; masses for

30 fabricating printing plates or silk-screen matrices; masses for fabricating structural materials.

With regard to light sources, the photopolymerisation process can use medium, low or high pressure mercury vapour lamps, super-35 actinic lamps or lamps specially designed to obtain high radiation intensity at wavelengths between 250 and 450 nm.

The photoinitiator systems according to the present invention are used in a quantity of between 0.1 and 15% by weight of the photopolymerisable mixture, and preferably between 0.5 and 10% by weight. The ratio of component A to component B can vary between 5 0.1 and 10 but values of between 0.5 and 1.5 are preferred.

When the compounds of formula I are used as the benzophenone system of type A, three advantages are obtained over the use of benzophenone itself, namely better photochemical efficiency and 10 less film coloration and odour.

When liquid mixtures of compounds of formula I with benzophenone are used, in addition to the stated advantages the preparation of photopolymerisable mixtures takes less mixing time and lower 15 temperatures can be used. In addition the fact that a liquid photoinitiator is used helps to keep the viscosity low and allows co-solubilisation of components which would otherwise be more difficult to dissolve.

20 The following examples illustrate the invention in greater detail, but without limiting it (the parts are by weight).

The benzophenones used are indicated by abbreviations and have the following characteristics:

25 BF = benzophenone - crystalline solid, M.P. 49°C, IR spectrum (KBr) : 1655, 1275, 695, 633 cm^{-1} .

TMB = 2,4,6-trimethylbenzophenone - metastable liquid, B.P. 189°C (17 mmHg) or crystalline solid with M.P. 35.5°C, IR spectrum (KBr) : 1670, 1270, 917, 710 cm^{-1} .

30 TEB = 2,4,6-triethylbenzophenone - liquid, B.P. 210-220°C (40 mmHg), IR spectrum (liquid film) : 1660, 1270, 925, 865, 705 cm^{-1} .

TIPD = 2,4,6-triisopropylbenzophenone - crystalline solid, M.P. 98-99°C, IR spectrum (KBr) : 1665, 1250, 950, 930, 880, 35 725 cm^{-1} .

PMB = 2,3,4,5,6-pentamethylbenzophenone - crystalline solid, M.P. 134-135°C, IR spectrum (KBr) : 1670, 1210, 890, 705

cm⁻¹.

TMOB = 2,4,6-trimethoxybenzophenone - crystalline solid, M.P. 112-113°C, IR spectrum (KBr) : 1660, 1600, 1585, 1125, 810 cm⁻¹.

5 MDEA = N-methyldiethanolamine - liquid.

EXAMPLE 1

Eutectic mixture of 2,4,6-trimethylbenzophenone and benzophenone (BF/TMB)

10

585 g of 2,4,6-trimethylbenzophenone (M.P. 35.5°C) are heated to 45°C, 415 g of benzophenone (M.P. 49°C) are added, and after agitation for 15 minutes the mixture is cooled to 20°C. A composition is obtained (molar ratio TMB/BF = 1.155) having the following characteristics; IR spectrum (liquid film) : 1660, 1270, 905, 700 cm⁻¹; clear liquid up to 10°C; pour point (ASTM D97/66) less than -10°C; Brookfield viscosity RVT 1/20 rpm = 55 mPas at 20°C, $\eta = 145$ mPas at 10°C.

20 EXAMPLES 2 to 5

The photo-crosslinkable mixtures having the composition indicated in the individual examples given hereinafter were applied to a glass plate to a thickness of 50 microns. After exposure to air for 30 seconds the films were irradiated by successive passages 25 at the indicated conveying speed under a medium pressure mercury vapour lamp of the indicated power at a distance of 10 cm from the light source. Sward hardness (ASTM D2134-66) and yellowing (ASTM D1925-63T) were determined.

30 The thermal stability, evaluated for photoinitiated mixtures kept in darkness at 60°C, was greater than 30 days for all the photoinitiator systems.

In Example 2, the operating conditions and results were as 35 follows:

Photo-crosslinkable composition	Laromer® LR 8496 (acrylated aliphatic epoxy resin BASE) (B)	95-93
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		MDEA	1-3
		Benzophenone compound (50% solution in 1,6-hexanediol diacrylate) (A)	4
	Lamp power	40 V/cm	
5	Conveying speed	20 m/min.	

	A	MDEA	R	Film tacki-	Sward hardness after			Yellowing Index
				parts	parts	ness after	2 passages	
		by wt	by wt	1 passage				
10	BF (a)	1	95	liquid	6	10	14	5
		2	94	tacky	8	12	14	6
		3	93	slightly tacky	10	10	14	6
	TMB	1	95	tacky	8	12	16	3
		2	94	slightly tacky	10	12	16	3
15		3	93	dry	10	12	16	3
	BF/TMB	1	95	slightly tacky	8	12	14	4
		2	94	dry	8	12	16	4
		3	93	dry	10	12	16	4

(a) BF was used for comparison purposes

20

In Example 3, the operating conditions and results were as follows:

	Photo-crosslinkable composition	Laromer® EA 81 (acrylated aromatic epoxy resin BASF) (R)	86
25		1,6-hexanediol diacrylate (HDDA)	0-12.25
		benzophenone compound (50% solution in HDDA) (B)	1-8
		MDEA	0.75-6
	Lamp power	40 V/cm	
30	Conveying speed	20 m/min.	

	B	B	MDEA	HDDA	Sward hardness after							
					parts	parts	parts	1 passage	2 passages	3 passages	4 passages	5 passages
					by wt	by wt	by wt					
35	BF (a)	1	0.75	12.25	tacky	2	6	6	6	8		
		2	1.5	10.50	12	18	20	24	24	24		
		4	3.0	7.0	12	20	24	26	26	30		

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	8	6.0	-	8	16	20	26	28
	TMB	1	0.75	12.25	8	10	12	12
		2	1.5	12.50	16	22	22	28
		4	3.0	7.0	14	24	28	32
5		8	6.0	-	12	22	26	30
	BF/TMB	1	0.75	12.25	4	8	10	10
		2	1.5	10.50	12	18	22	26
		4	3.0	7.0	14	22	28	30
		8	6.0	-	12	20	12	28
10	PMB	2	1.5	10.50	-	22	22	26
	TIPB	2	1.5	10.50	-	18	22	24
	IMDA	2	1.5	10.50	-	16	20	24

(a) BF was used for comparison purposes

15 In Example 4, the operating conditions and results were as follows:

Photo-crosslinkable composition	Laromer® EA 81 benzophenone compound (16.2% solution in vinylpyrrolidone) (B)	86
20 MDEA		11
Lamp power	40 W/cm	3
Conveying speed	20 m/min.	

25	B	Sward Hardness after:			
		1 passage	2 passages	3 passages	4 passages
	BF (a)	22	30	32	38
	TMB	24	32	38	40
	TIPB	18	32	38	40
	PMB	20	30	36	38
30	IMDA	26	28	34	38

(a) BF was used for comparison purposes

In Example 5, the operating conditions and results were as follows:

35	Photo-crosslinkable composition	Laromer® 55 F (acrylated polyester resin BASF) benzophenone compound (A)	100
			2

- 10 -

Silicone Dow DC 190 (20% solution)
in xylene) 0.2
Film thickness 500 microns
Lamp power 80 V/cm

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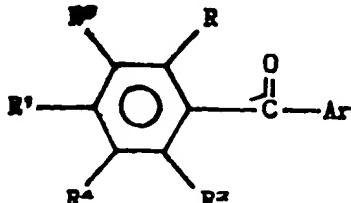
Yellowing index of crosslinked film after:		
	1 passage at 3.5 m/min	10 passages at 1 m/min
BF (a)	2	15
TMB	2	10
10 2,2-dimethoxy-2-phenylacetophenone (b)	10	20
<u>1-benzoylcyclohexanol (b)</u>	<u>5</u>	<u>12</u>

(A) used for comparison purposes

(b) non-benzophenone compounds used for comparison purposes.

PATENT CLAIMS

1. As initiators for the photopolymerisation of ethylenically unsaturated compounds, the use of systems consisting of:
 5 A) one or more benzophenones of formula I



10

in which

R signifies linear or branched C_1-C_{12} alkyl possibly substituted with one or more phenyl, chlorine, bromine, C_1-C_{12} alkoxy, ArO^- , $ArSO^-$, $ArSO_2^-$, C_1-C_{12} alkylsulphinyl or C_1-C_{12} alkylsulphonyl groups; or $-SO_3H$ or C_1-C_{12} dialkylamino, respectively as free acids or bases or salified with organic or inorganic bases; C_1-C_{12} alkoxy; or ArO^-

15 R' , R'' which can be equal or different, each independently have the same meaning as R or represent hydrogen or a bridge of carbon atoms with Ar or R^3 or R^4 possibly comprising heteroatoms

20 R^3 , R^4 which can be equal or different, each independently represent hydrogen, linear or branched C_1-C_{12} alkyl, phenyl, chlorine, bromine, $-SO_3H$ possibly salified with organic or inorganic bases, or $ArCO^-$

25 Ar represents a C_6-C_{10} aryl either non-substituted or carrying one or more substituents of the halogen, C_1-C_{12} alkyl, phenyl, C_1-C_4 alkoxy, C_3-C_6 cycloalkoxy, phenoxy, $-COOH$, C_1-C_6 alkoxy carbonyl, benzoyl, C_1-C_6 dialkylamino, C_1-C_6 alkylthio, alkylsulphinyl, alkylsulphonyl, arylthio, arylsulphinyl and arylsulphonyl group; or 2,3 or 4-pyridyl; or a furan or thiophene residue

30 B) an organic tertiary amine of aliphatic type, or an ester of p-dimethylaminobenzoic acid or 4,4'-bis-(C_1-C_6 dialkylamino) benzophenone, or single or polymeric ethers of primary or secondary alcohols or glycols or primary or secondary

aliphatic alcohols.

2. The use in accordance with claim 1 of systems consisting of:

5 A) one or more benzophenones of formula I in which R, R¹, R² which can be equal or different, each independently signify C₁-C₄ alkyl,
R³, R⁴ which can be equal or different, each independently signify hydrogen, C₁-C₄ alkyl, or -SO₂H possibly
10 salfied with organic or inorganic bases,
Ar signifies phenyl, possibly substituted with one or more C₁-C₄ alkyl, Cl, Br or C₁-C₄ alkylthio groups
B) an organic tertiary amine of aliphatic type, or an ester
of p-dimethylaminobenzoic acid or 4,4'-bis-(C₁-C₄ dialkylamino)
15 benzophenone, or molecules containing single or polymeric
derivatives of glycols.

3. The use in accordance with claims 1 and 2 of systems consisting of:

20 A) one or more benzophenones of formula I chosen from 2,4,6-trimethylbenzophenone; 2,4,6-triethylbenzophenone; 2,4,6-triisopropylbenzophenone
B) tertiary amines, or alcohols or ethers as defined in
claim 1.

25

4. The use in accordance with claims 1, 2 and 3 of systems in which component A consists of one or more compounds of formula I, preferably chosen from 2,4,6-trimethylbenzophenone, 2,4,6-triethylbenzophenone, 2,4,6-triisopropylbenzophenone and

30 2,3,4,5,6-pentamethylbenzophenone, in mixture with benzophenone, said mixture having a melting point considerably lower than that of the individual components.

35 5. The use in accordance with claims 1, 2, 3 and 4 of systems in which component A consists of a mixture of 2,4,6-trimethylbenzophenone and benzophenone in a molecular ratio of between 10:1 and 1:10 and preferably between 1.3:1 and 1:1, said

mixture being liquid above 10°C.

6. A photopolymerisable system consisting of:
 - a) ethylenically unsaturated monomers and/or oligomers
5 preferably of acrylic or methacrylic type,
 - b) mixtures of benzophenones and tertiary amines as photochemical polymerisation initiators defined as in claims 1 to 5,
 - c) other compounds such as pigments, fillers, dyes,
10 stabilisers and various auxiliaries.
7. A mixture consisting of 2,4,6-trimethylbenzophenone and benzophenone in a molecular ratio of between 1.3:1 and 1:1, having the characteristic of being liquid at temperatures
15 exceeding 10°C.



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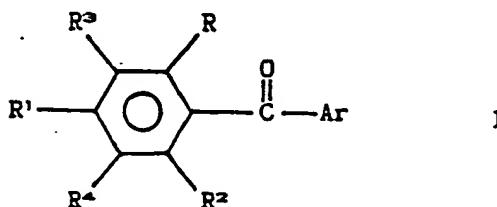
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⑮ Substituted benzophenones and their liquid mixtures suitable for use as photopolymerisation initiators.

⑯ As initiators for the photopolymerisation of ethylenically unsaturated compounds, the use of systems consisting of compounds of benzophenone type of formula I



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in which R, R¹ and R² are preferably alkyls of 1-4 carbon atoms, R³ and R⁴ are preferably hydrogen and Ar is preferably phenyl, in combination with donors of hydrogen or substances which determine the formation of labile photochemical complexes, such as alcohols, ethers and tertiary amines with hydrogens in the alpha position, and the use for the same purpose of mixtures of 2,4,6-trialkylbenzophenones and benzophenone and particularly of a mixture of 2,4,6-trimethylbenzophenone and benzophenone in a molar ratio of 1.155, which has the advantage of being liquid at temperatures exceeding 10°C and of possessing photochemical activity superior to that of benzophenone.



EP 86 10 9669

DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl 4)						
A	US-A-4 071 424 (E.C. DART et al.) ---		C 08 F 2/50 G 03 C 1/58						
A	US-A-4 080 275 (J.A. PHOTIS et al.) ---								
A	US-A-3 686 084 (H.J. ROSENKRANZ et al.) -----								
			TECHNICAL FIELDS SEARCHED (Int. Cl 4)						
			C 08 F G 03 C						
<p>The present search report has been drawn up for all claims</p> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33%;">Place of search</td> <td style="width: 33%;">Date of completion of the search</td> <td style="width: 34%;">Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>22-01-1987</td> <td>CAUWENBERG C. L. M.</td> </tr> </table> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>				Place of search	Date of completion of the search	Examiner	THE HAGUE	22-01-1987	CAUWENBERG C. L. M.
Place of search	Date of completion of the search	Examiner							
THE HAGUE	22-01-1987	CAUWENBERG C. L. M.							